Ultraviolet Photo-detective Characteristics of Al/LPD-Oxide/n-type GaN with Photo-electro-chemical Wet Etching-based Rough GaN

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Abstract

A room-temperature anisotropic photo-electro-chemical etching process for n-type GaN films using a potassium hydroxide (KOH, pH=1.09~1.39) and phosphoric acid (H_3PO_4, pH=12.60~12.90) in the stirrer solution and Deuterium lamp illumination is described. The process provides anisotropic etch profiles and high etch rates >240 nm/ min at moderate light intensities ~17.3 mW/cm^2 @237 nm in the H3PO4 (pH=1.09) solution. The etch rate and photocurrent are characterized as a concentration of the stirred solutions. In this work, two types of metal-oxide-semiconductor (MOS) structures were fabricated. One is the semiconductor layer with as-grown n-GaN (Sample B), and the other is the n-GaN surface with photo-electro-chemical etching (Sample A). The oxide layer for both these devices were fabricated using silicon dioxide insulator grown by a low-temperature (30-40℃) and reliable method of liquid phase deposition (LPD). For an incident light wavelength of 366 nm with an intensity of 4.15 mW/cm^2 and a 6 V reverse bias, it was found that the photo to dark current ratio was around 31 and 26 for sample A and B, respectively. The photo to dark current ratio of sample A increases 19.2% compares with sample B.

Keywords

Wet Etching; Photo-detective;GaN; Liquid Phase Deposition

Introduction

In recent years, wide direct bandgap semiconductor gallium nitride (GaN) and its ternary alloys were applied in high-power or high-frequency optoelectronic devices, such as p-i-n and p-π-n photodiode[Monroy et al.,(1999), Monroy et al. (1997)]. The ultraviolet (UV) rays photo-detectors have been the subject of a vast body of the research work[Hwang et al. (2005)].

Obviously, the fundamental step in any devicesis the transfer of patterns onto the surface of the semiconductor by etching. The removal of surface material is a fundamental device processing step, and the most successful etching of GaN has been accomplished using dry etching methods, including reactive ion etching (RIE), inductively coupled plasma (ICP), electron cyclotron resonance (ECR) [Youtesy et al.(1997), Hwang et al.(2004)]. Dry etching techniques generally utilize a strong physical etch component, which can lead to ion-induced damage of the semiconductor. To improve the performance of such devices, their structures must be fabricated with damage-free from etching. Wet chemical etching is an important complement to dry etching methods by providing low damage etching, low cost and selective etching of different materials. A photo-electro-chemical (PEC) etching was considered to etch with slight damage for the fabrication of GaN devices, rather than ion sputtering that inevitably causes surface damage.

Minsky et al have reported localized electrochemical etching of unintentionally n-type GaN layers using HeCd laser illuminations (325 nm) and KOH solutions[Peng et al.(1998)]. By controlling the etching parameters, such as electrolyte concentration, illumination intensity, photocurrent, which affect the morphology of the etched surface and the etch rate can be obtained. A detailed description of the PEC system and wet etching process has been reported elsewhere [Rotter et al. (2000), Riedl et al (2003)].

Experiment Details

In this paper, we report a series of PEC etching experiments on the n-type GaN in which we have used deep ultraviolet (λ=237 nm) illumination to study the wet etching process in electrolytes of different concentrations KOH and H_3PO_4stirrer solutions. A 30W Deuterium lamp (Oriel) was used as UV light source. Further, GaN MOS ultraviolet photo-detector were fabricated using silicon dioxide insulator grown at a low-temperature (30-40℃) and reliable method of liquid phase deposition (LPD). The etch depth and the profile of the illuminated spots were characterized by a Tencor Alpha-step 500 profilometer and by an atomic force microscope (AFM). Material and electrical properties of LPD-SiO_2 on GaN were investigated by using energy dispersive X-rays (EDX). An ultraviolet Xe lamp at wavelengths of 366 and 254 nm was used as an optical source and the current-voltage (I-V) behavior was measured using an HP 4155B analyzer.

Results and Discussion

The n-GaN layer was grown on a c-face sapphire substrate by a metalorganic chemical vapor deposition (MOCVD) system with a horizontal reactor. Detail growth method has been reported previously [Hwang et al.(2005)]. In our study, GaN was obtained with a carrier concentration of ~$2x10^{17}$ cm^{-3} and a mobility of ~250 cm^2/V-s. Next, the n-type GaN sample was cleaned by being dipped into an HCl:H_2O (1:1) solution for 5 min and a Ti layer (100nm) was deposited by Joule evaporation. The pattern of the metallization was defined by standard metal lift-off techniques. Subsequent annealing in N_2 ambient at 850℃ for 3.5 min is applied to form ohmicTiN contacts. The Ti served to provide electrical contact to the sample as well as an etch mask. FIG.1 shows the experimental apparatus used in this work.

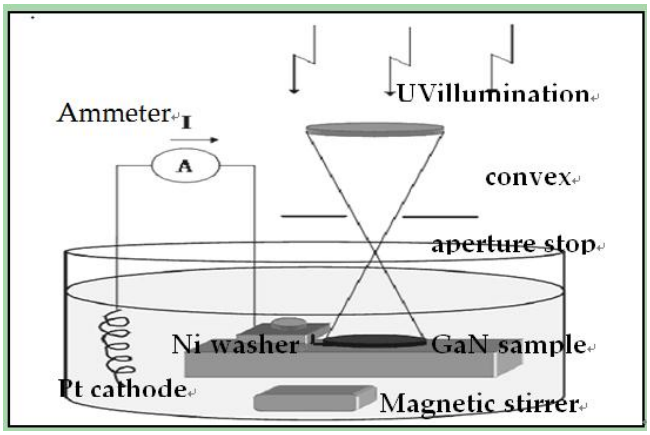

FIG. 1SCHEMATIC OF ETCTING APPARATU

The samples were clipped to a Teflon base using a nickel washer. A Pt wire was used as the system cathode. No bias was applied between the sample and the Pt cathode. An ammeter was used to monitor the current flowing within the electrochemical cell. A positive lens is to be used as a light beam converges, andthe sample is placed at the focal plane of the positive lens. Using an aperture stop (pinhole) determines the amount of light reaching the sample. An unfiltered Deuterium lamp provided uniform illumination over the entire surface of the sample with an intensity of ~17.3mW/cm^2 at the wavelength of 237 nm. Precautions were taken to refrain from the UV induced absorption in the electrolytes by utilizing a short optical path about 1.5 mm in liquid. The electrolyte consisted of dilute aqueous solutions of KOH and $H_3PO_4$with concentrations in the range of pH=1.09~1.39 and pH=12.60~12.90, respectively. The solutions were magnetically stirred during the etching. UV illumination was used to generate electron-hole pairs at the semiconductor surface, which enhanced the oxidation and reduction reactions within an electrochemical cell. As the electron-hole pairs have generated, it is important that holes are transported to the semiconductor surface weakening the chemical bonds, thus encouraging dissolution, and additionally the electrons are swept to the cathode to avoid subsequent recombination with the holes at the surface. The resultant photocurrent is therefore proportional to the reaction rate of the hole-assisted etching at the semiconductor-electrolyteinterface[Youtsey et al. (1998)]. The PEC process, the UV excited hot carriers at the GaN/electrolyte interface have excess energy to access the H^+/H_2 and OH^-/O_2 redox levels in the water and to enhance the oxidation process. The oxide layer is subsequently dissolved in acids or bases of suitable low concentration[Penga et al. (1998)]. Youtsey et al, has postulated that the following both reactions

(oxidation and oxide dissolution) are responsible for the decomposition of GaN. Thus,

$$2GaN + 6h^{+} + 6OH^{-} \rightarrow Ga_2O_3 + 3H_2O + N_2 \uparrow \quad (1)$$

$$Ga_2O_3 + 6OH^{-} \rightarrow 2GaO_3^{-} + 3H_2O \quad (2)$$

The holes drift to the semiconductor surface, where they oxidize the gallium nitride, thus producing N_2 bubbles that have been observed and Ga_2O_3 that dissolvesaway[Youtesy et al. (1997)]. During the overall photo-assisted electrochemical process, the etching of n-type GaN results when the rate of dissolution of oxidized products is faster than that of the oxide formation. FIG.2 shows the photo-current conducted through the electrochemical cell during a 60 min etch. The onset of illumination corresponded with an approximately exponentially decrease in photo-current flow within 20 min. According to Faraday's law of electrolysis, the photo-current flow between anode (GaN sample) and cathode (Pt) is proportional to the reaction rate at the semiconductor/electrolyte interface. We suggest the total reaction rate is limited by diffusion.

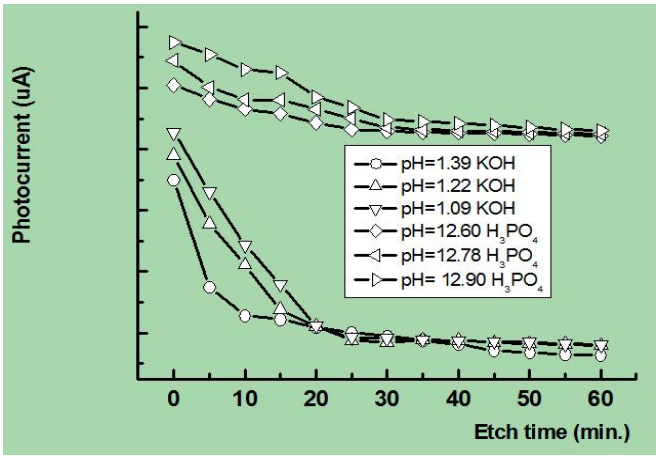

FIG. 2 PLOT OF TIME EVOLUTION OF PHOTOCURRENT

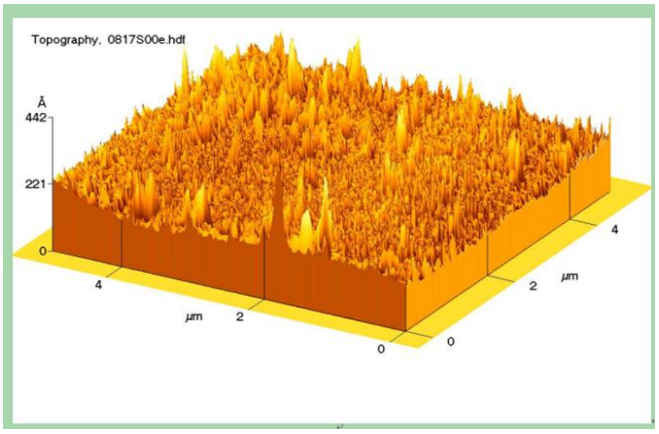

FIG. 3 AFM IMAGES OF A GaN SURFACE (KOHPh=12.9) WITH APERTURE STOP 0.7μm ETCHDEPTH 60 MIN ETCH TIME ROUGHNESS 23.7 nm.

FIG.3 shows a AFM images of a n-type GaN surface obtained a uniform and smooth etched surface was obtained with a root-mean-square (RMS) roughness 23.7 nm in the stirrer solution (pH=12.9 KOH) with aperture stop.FIG.4 shows a AFM images of a n-type GaN surface obtained a uniform and smooth etched surface was obtained with a root-mean-square (RMS) roughness 15.1 nm in the stirrer solution (pH=1.09H_3PO_4) with aperture stop. FIG.5 shows an instantaneous measure of the etch rate of the semiconductor. The etch rate gradually decreases due to the decrease in photo-current flow within 15 min. We believe the oxide dissolution rate equals the oxidation rate of the underlying n-type GaN film, andthe photocurrent levels out within 43~60 min, as shown in FIG.2. We have presented the applicability of PEC etching to the surface of n-type GaN at room temperature. The process provides highly anisotropic etch profiles and high etch rates >240 nm/min at moderate light intensities ~17.3mW/cm² @237 nm by Deuterium lamp in the H_3PO_4 (pH=1.09) solution.

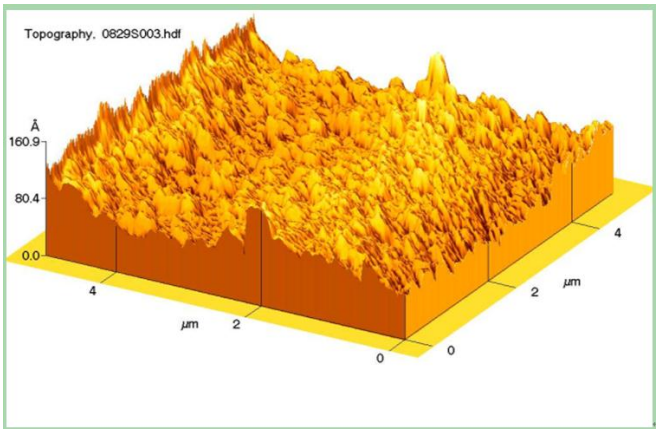

FIG. 4 AFM IMAGES OF A GaN SURFACE (H3PO4 pH=12.9) WITH APERTURE STOP 1.83 μm ETCH DEPTH 60 MIN ETCH TIME ROUGHNESS 15.1 nm.

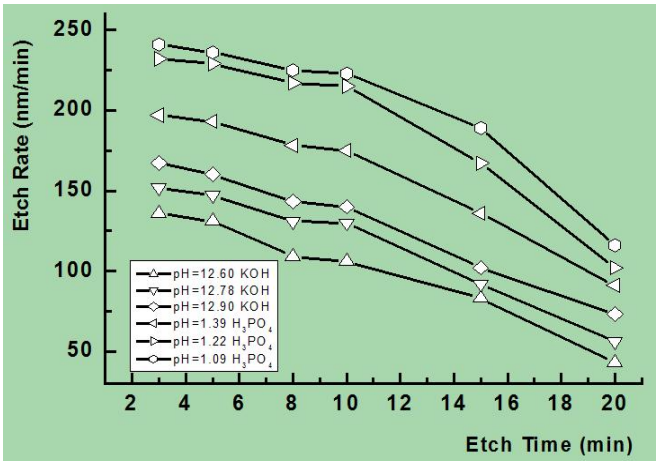

FIG.5 SHOWS AN INSTANEOUS MEASURE OF THE ETCH RATE OF THE SENICONDUCTOR

The ultraviolet photo-detector Al/LPD-Oxide/n-type GaN with photo- electro-chemical wet etching-based rough GaN (sample A) and Al/LPD-Oxide/as grew n-type GaN (sample B),which were fabricated using silicon dioxide insulator grown by a low-temperature (30-40℃) and reliable method of liquid phase deposition (LPD). The LPD process uses a supersaturated acid aqueous solution of hydrofluosilicic (H_2SiF_6) as a source liquid and an aqueous solution of boric acid (H_3BO_3) as a deposition rate controller, which has been described in detail elsewhere [Yang et al.(2011)12]. The chemical reaction of LPD process can be expressed in the following.

$$H_2SiF_6 + 2H_2O + \Delta H \leftrightarrow 6HF + SiO_2 \downarrow \quad (3)$$

$$H_3BO_3 + 4HF \leftrightarrow BF^- + H_3O^+ + 2H_2O \quad (4)$$

In this study, the different concentrations of H_2SiF_6 and H_3BO_3 variedfrom 0.3 to 1M and 0.005 to 0.01M, respectively. Al/LPD-SiO_2/n-type GaN MOS photo-detectors were fabricated by using standard lithography and lift-off technique. Ohmic contact of Ti/n-GaN metals and the gate electrode of Al were formed into a SiO_2 film by evaporation. FIG.6 shows the fabricated ultraviolet photo-detector structure of Al/LPD-Oxide/n-type GaN(sample A and B). The thickness of silicon dioxide film, measured by ellipsometry and derived by assuming the silicon dioxide refractive index of 1.43, ranged from 30 to 55 nm. In FIG.7 the element analysis of LPD-SiO_2, deposited into n-type GaN, is investigated by using EDX. In addition to Ga and N peaks, the Si and O peaks are found in our LPD-SiO_2 films, demonstrating the SiO_2 was grown into GaN layer successfully. For photocurrent measurements, a Xe lamp and a mono-chromator emitting at 366 and 254 nm were used, as the optical source with an intensity of 4.15 mW/cm².

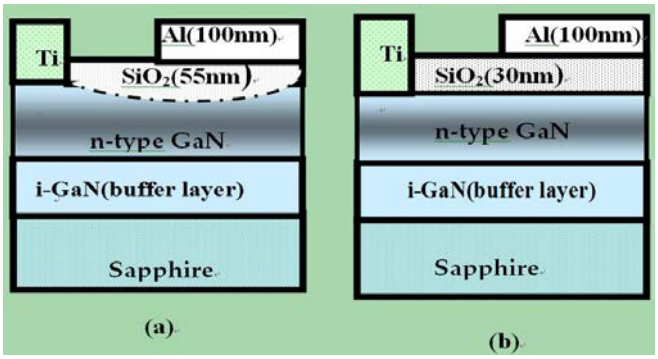

FIG. 6 THE FABRICATED MOS PHOTO-DETECTOR STRUCTURE (A) Al/LPD-OXIDE/N-TYPE GaN WITH PHOTO-ELECTRO-CHMICAL WET ETCHING-BASED ROUGH GaN (SAMPLE A) (B) Al/LPD-OXIDE/AS GROWN N-TYPE GaN (SAMPLE B)

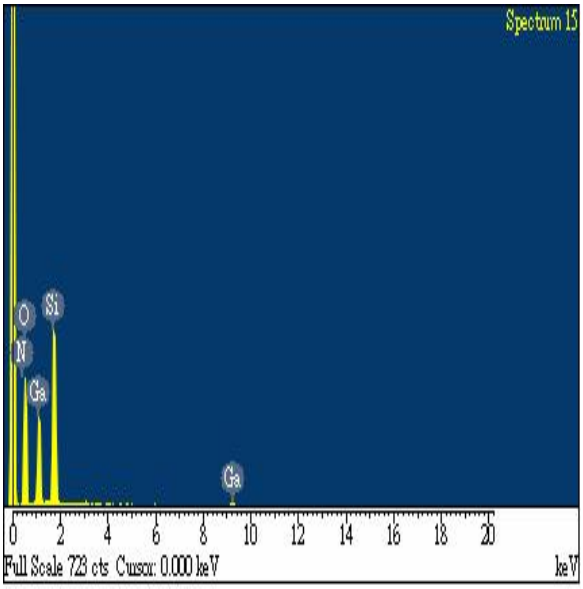

FIG. 7 ELEMENT ANALYSIS OF LPD-SiO_2 BY USING EDX

FIG.8 shows the current densities vs different reverse bias for dark and photo-illuminated MOS photo-detector with LPD-SiO_2 insulator. We attribute the current transport in our device to defect-assisted tunneling. The band diagram is for which shown in FIG.9. For an incident light wavelength of 366 nm with an intensity of 4.15 mW/cm² and a 6 V reverse bias, it was found that the photo to dark current ratio was around 31 and 26 for sample A and B, respectively. The photo to dark current ratio of sample A increases 19.2% compared with the sample B.

We suppose the photo-electro-chemical wet etching-based rough GaN which was applied in photo-detector structures as an anti-reflection coating. The surface of rough GaN substantially reduces reflection losses and increases absorption probability in the device; however, for an incident light wavelength of 254 nm with an intensity of 4.15 mW/cm² and a 6 V reverse bias, it was found that the photo to dark current ratio was around 11 and 15 for sample A and B, respectively. The photo to dark current ratio of sample A is even smaller than that of sample B This behavior can be attributed to absorption in the metal gate layer or SiO_2 insulator layer, because the penetration depth is very shallow a wavelength of 254 nm. Thus, only few 254 nm photons are absorbed in the depletion layer where photocurrent is generated.

FIG.10 shows an incident light wavelength of 366 nm with an intensity of 4.15 mW/cm² and a 6 V reverse bias, and it was found that the measured responsivity was around 0.145 and 0.116 A/W for sample A and B, respectively. We have demonstrated the

photo-electro-chemical wet etching-based rough GaN which was applied UV photo-detector MOS structures as an anti-reflection coating.

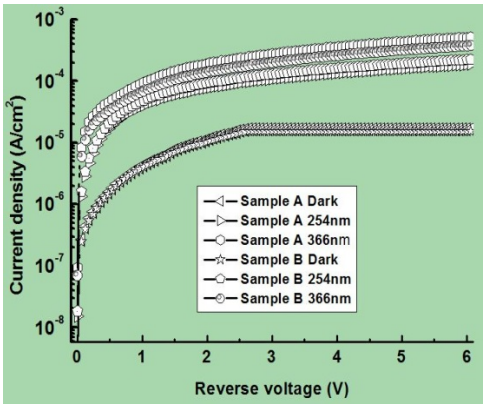

FIG.8 THE CURRENT DENSITIES VS DIFFERENT REVERSE BIAS FOR DARK AND PHOTO-ILLUMINATED MOS PHOTO-DETECTORS

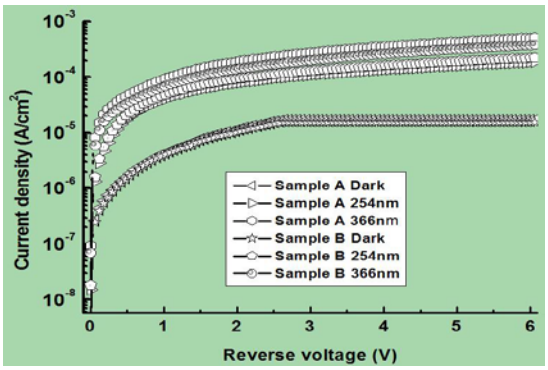

FIG. 9 BAND DIAGRAM FOR DEFECT-ASSISTED TUNNELING. THE HOLES TUNNEL THROUGH DONOR-LIKE DEFECTS IN LPD-SiO2 TOWARD THE METAL GATE ELECTRODE

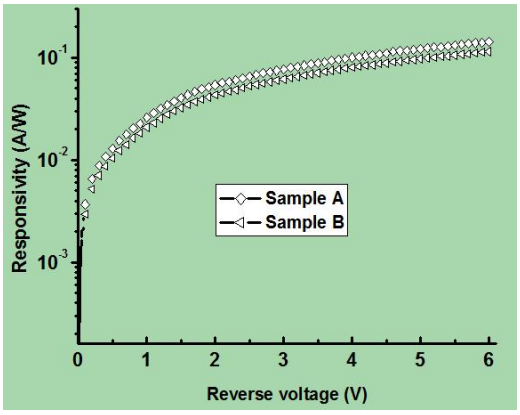

FIG. 10 THE RESPONSIVITY VS DIFFERENT APPLIED BIAS FOR PHOTO-ILLUMINAYED MOS PHOTO-DETECTOR

Conclusions

We report a study of the deep ultraviolet irradiation effects on the wet chemical etching of n-typeGaN. The process provides highly anisotropic etch profiles and high etch rates >240 nm/min at moderate light intensities ~17.3mW/cm² @237 nm by Deuterium lamp in the H_3PO_4, solution. The sample A is the n-GaN surface with photo-electro-chemical etchingin which the photo to dark current ratio increases 19.2%.

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